AMENDMENTS TO THE SPECIFICATION

I. Please replace the original TITLE with the following amended TITLE:

OXYGEN-REMOVING PRE-PROCESS FOR COPPER INTERCONNECTS GROWN BY ELECTROCHEMICAL DISPLACEMENT DEPOSITION

II. Please replace the original SPECIFICATION, Pages 1-6, with the following amended SPECIFICATION:

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to ~~an oxygen removing pre-process~~ a pre-process which expels the oxygen in the deionized water, DI water, before preparing the displacement plating solution for copper interconnects ~~grown, and more particularly to an oxygen removing pre-process for copper interconnect~~ grown by displacement reaction, and more particularly by electrochemical displacement deposition (EDD).

2. Description of Related Art.

~~The convention~~ There have been many methods of growing copper films or interconnects growth for circuits of very large scale ~~integrated circuit~~ integration (VSLI) and ultra large scale integration (ULSI). ~~integrated circuit comprises~~ They can be classified into physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, and electroless deposition, etc. ~~, wherein the copper formed by other methods.~~ However, there are several disadvantages found in these methods. ~~the~~ In the case of PVD, the step coverage of the copper grown in the grooves ~~in~~ on the surface of the wafer ~~by PVD~~ is not even. ~~, and the~~ The copper film grown by CVD can be conformal ~~grown by CVD has a good coverage, but not pure such that~~ while it contains too many impurities ~~the copper grown by CVD~~ such that it has a very high resistance ~~higher than that of the copper grown by PVD~~. Furthermore, the ~~prescription of~~ popular dry etching process cannot be adopted to remove the unwanted copper due to the corresponding ~~create a reactant~~ product is non-volatile and is not easily exhausted out of the wafer. ~~with high volatility such that the copper film cannot be etched and formed leading wires on the surface of the wafer. Consequently, major manufacturers~~ Currently, the ~~use damascene~~ Damascene process and its variations are predominantly used to ~~grow~~ form copper wires for modern integrated circuits (ICs).

The ~~However, the damascene~~ Damascene process utilizes the chemical-mechanical polish (CMP) process to remove the unwanted portion of copper.

However, the process steps are complicate and the throughput is low. ~~has complicated steps and a less output such that many manufacturers try to use~~ Some researchers proposed low-cost the methods ~~of~~ such as electroplating and electroless deposition to increase the throughput. ~~alter the processes for growing copper on the surface of the wafer because the electroplating and electroless deposition have a economy manufacturing cost.~~ However, there was a concern about the ~~the electroplating~~ plating agents which will pollute the products and the environment, ~~in which we live and~~ And the obtained resistance, the step coverage and the quality of ~~crystal of~~ the grown copper still need to be ~~promoted such that to use the methods of electroplating and electroless deposition to alter the processes of growing copper is not extensively excepted~~ improved.

The electrochemical displacement deposition (EDD) ~~is provided~~ has been proposed recently to grow copper ~~recently~~ with a solution containing popular chemicals used in IC fabrication processes. The EDD process is utilized ~~is provided~~ as a pre-process ~~of electroplating copper and electroless depesition~~ copper to create a seed layer for later growth of thick copper layers by the electroplating method or the electroless deposition. ~~promoting the quality of crystal and the resistance of the grown copper.~~ However, the copper grown by the method of the EDD also has a high resistance and is difficult to ~~be adhered~~ adhere on the surface of the wafer, ~~such that a~~ An annealing process is ~~necessary~~ usually used to reduce the resistance of the copper film ~~formed by the EDD~~.

The present invention has arisen to mitigate and/or obviate the possibility of ~~disadvantages of the conventional methods for copper interconnect grown~~ high resistance for the copper obtained in the chemical plating method, especially the EDD method.

SUMMARY OF THE INVENTION

The main objective of the present invention is to provide an ~~improved~~ oxygen-removing pre-process for copper ~~interconnect~~ grown ~~by electrochemical~~ from "cleaned" chemical solutions ~~displacement deposition~~ to ~~get a low electric~~ reduce the resistance of the copper. Before preparing the chemical reaction, the DI water is first heated to boil to reduce the concentration of the oxygen in it. The oxygen-removed DI water is then cooled down to the room temperature in a sealed beaker. The electrochemical displacement solution is prepared in the "cleaned" water for later deposition of copper films. It has been found that the obtained copper has a lower resistance than that grown from the same solution without the oxygen-removing preprocess.

~~The achieve the objective, the oxygen-removing pre-process in accordance with the present invention is to remove the oxygen in the reaction solution before displacement and deposition a copper film/conducting wire such that the copper film/conducting wire is grown and has a lower electric resistance.~~

~~Further benefits and advantages of the present invention will become~~

~~apparent after a careful reading of the detailed description with appropriate reference to the accompanying drawings.~~ Detailed drawings and description about the treatment are shown and described below.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 ~~is a function view that~~ shows the effect of the annealing time on the sheet resistance of the copper film ~~formed~~ grown by the electrochemical displacement reaction without oxygen-removing preprocess, wherein the environment gas during annealing is H_2 and the annealing temperature is kept at ~~centigrade~~ 500 degrees centigrade; a long time, almost up to an hour, of high-temperature process is usually needed to improve the resistance of the copper made from the chemical reactions in electroplating or electroless processes;

Fig. 2 shows ~~is a~~ the process flow ~~chart~~ of the oxygen-removing pre-process ~~for~~ before preparing chemical solutions for copper ~~interconnect grown~~ deposition in ~~accordance with~~ the present invention; and

Fig. 3 ~~is a function view that~~ illustrates the resistivities of two samples, A and B, as-deposited ~~form the reaction solutions~~ from the EDD solution where sample A was grown in an EDD solution with the oxygen-removing pre-process and sample B was in the solution without the oxygen-removing pre-process. The resistivity of ~~, wherein the resistivities of A after~~ sample B after a post-annealing process in H_2 at 500 degrees centigrade for 50 minutes is also

demonstrated for comparison.

DETAILED DESCRIPTION OF THE INVENTION

High temperature annealing is a practice usually used in semiconductor processes to improve the quality of films. ~~With reference to~~ As seen in Fig. 1, it is really effective to introduce hydrogen ~~is injected~~ into the chemically grown copper films in a high-temperature furnace ~~that is kept at centigrade 500 degrees for annealing process~~. The cost is time and thermal energy. ~~As shown in~~ In Fig. 1, the resistance of copper film is gradually reduced ~~relative to~~ along with the processing annealing time, ~~such that we can~~ It is conjectured that the primary reason to degrade the resistance of ~~oxygen contained in~~ the copper film grown by chemical processes may be the oxygen in the solution. The oxygen can be absorbed in the newly formed copper films during the chemical reaction. ~~will raise the resistance of the copper film. Consequently, it is believed that oxygen is the primary factor deteriorating the resistivity of the copper film.~~ After annealing in H_2, the absorbed oxygen in the copper may react with H_2 at high temperatures to become water vapor and be exhausted out of the copper. As a result, the quality of the as-deposited copper films ~~is~~ can be further ~~excellent enough and there is no need of further annealing treatment~~ improved by annealing.

In this current invention, high-temperature annealing can be omitted if

the oxygen-removing preprocess is applied before preparing reaction solutions. ~~With reference to~~ Fig. 2 [[,]] shows one example for the ~~oxygen-removing pre-process in accordance with the present invention comprises the following~~ corresponding steps of the EDD method: [[,]]

~~1.~~ Step 1. ~~Preparing~~ Prepare a clean Teflon beaker (10) ~~that is high-purity cleaned~~.

~~2.~~ Step 2. ~~Adding~~ Pour ~~one~~ one-liter deionized water (2) into the beaker (10). The deionized water is used as a the solvent ~~to mixing reaction solution~~.

~~3.~~ Step 3. The ~~beaker (10) with the~~ deionized water (2) in the beaker (10) is heated by a heater (11) until boiling and is kept in boiling for two minutes. During the heating process, ~~The~~ the beaker (~~11~~10) is ~~in an~~ kept open ~~opened condition during being heated~~ for removing the oxygen easily going out of ~~that is dissolve in the deionized~~ water.

~~4.~~ Step 4. ~~Take~~Removing ~~the heater (11) from~~ the beaker (10) off from the heater (11) for cooling. ~~, closing~~ At this moment, the beaker (10) is sealed by a polypropylene film to prevent the oxygen in the air ~~form~~ being dissolved back into the ~~solution water and maintaining the~~ The beaker (10) is placed in a hood for about forty minutes to cool down to the room temperature ~~for cooling~~.

~~5.~~ Step 5. ~~Removing~~ Remove the polypropylene film and prepare the

reaction solution. The solution for EDD method consists of forty-milliliter buffered ~~adding~~ hydrofluoric (BHF) acid (or sometimes called buffered oxide etchant, BOE) ~~for forty milliliters~~ and four-gram cupric sulphate ($CuSO_4$) ~~for four grams into~~. The agents in the beaker (10) ~~and~~ is well mixed by stirring ~~the solution with~~ by a Teflon stick (13) ~~such that the solution of EDD is finished and almost containing no oxygen.~~

~~6.~~ Step 6. Perform the EDD reaction. A wafer (3) with a titanium ~~displacement~~ layer (31), patterned or blanket, is placed into the solution in the beaker (10) for eight minutes ~~to execute displacement process~~. A newly formed copper film (32) will take the place of the titanium (31).

~~7.~~ Step 7. Clean and dry. Take out the wafer (3) ~~and~~ where a ~~the~~ high quality copper film (32) ~~will~~ forms on the surface of the wafer (3 [[.]]).

The following steps give an example to manufacture ~~manufacturing processes of~~ the wafer (3) are before be put into the EDD solution ~~described as follow~~.

~~1.~~ Step 1. ~~Preparing~~ Prepare a Si -chip wafer of electronic grade, ~~that is high purity cleaned.~~

~~2.To grow~~ Step 2. Grow a wet oxide layer ~~that has a thickness~~ for of 1500 Å thick to isolate the upper conducter layers from the lower substrate ~~for insulating in a high temperature stove~~.

~~3.~~ Step 3. Grow another thin insulating layer to resist the attacks of HF

during in the chemical reaction. This layer can be selected as ~~To grow~~ a Si_3N_4 ~~layer that has~~ having a thickness ~~for~~ of 500 Å ~~for insulating and anti-corroded~~ grown by PECVD.

~~4.~~ Step 4. ~~To grow~~ Grow a thin adhesive layer of TiN by a sputtering system. Its thickness is ~~have a thickness for~~ 100 Å. This layer is used to enhance ~~for strengthening~~ the ~~adhering effect~~ adhesion between the ~~Ti~~ upper metal layer and the underlying insulating layer, i.e. Si_3N_4 in this example ~~by using a sputtering system~~.

~~5.~~ Step 5. Grow a sacrificial layer to be replaced in the displacement reaction. ~~To grow a~~ Ti can be used in this step by ~~metal displacement layer by using a~~ sputtering ~~system, the Ti metal displacement layer has a~~ Its thickness depends on the desired copper. Thicker sacrificial layer will give a thicker copper layer. It is selected as ~~for~~ 3000 Å in this example.

The wafer (3) ~~as~~ manufactured by the above process ~~can get a better effect after the method of~~ is put into the EDD solution in which the DI water has been treated previously by ~~in accordance with~~ the present invention. The copper ions in the chemical solution will be reduced to form copper adatoms to displace the Ti atoms. The Ti layer will be gradually replaced by the new copper layer. The reaction will stop after all of the Ti layer is consumed. The sample (2) is then taken out of the plating bath and then cleaned by DI

water and is dried by a N_2 gun.

In our experiment, it was found that ~~The~~ the obtained copper films or ~~the copper conducting~~ wires has have a very low electric resistance. ~~With reference to the point B in~~ Fig. 3 [[,]] shows the average electric resistance of the copper ~~growing~~ grown from the EDD solution. In this figure, point B is the resistance of the copper grown from the EDD solution prepared by the method of the present invention. The average value is was 1.96 [[i]] μΩ-cm that is very close to the ideal value (1.67 [[i]] μΩ-cm) of bulk copper. Point A indicates the resistance of the copper grown from the EDD solution without the oxygen-removing preprocess. Comparing these two values, the effect of the oxygen-removing preprocess, the current invention, is significant in improving the quality of the chemically grown EDD copper. High-quality EDD copper can be obtained from the solution using the oxygen-removing pre-process, the invention, without a long time of high-temperature post-annealing. ~~To compare with the electric resistance of the copper film growing by the conventional method, the point A in Fig. 3, the electric resistance of the copper growing by the method of the present invention has is greatly lower than that of the copper that grows using the conventional method.~~ Consequently, conventional ~~the~~ high-temperature annealing processes is can be omitted in improving the quality of the chemical copper ~~unnecessary relative to the present invention~~.

Although the invention has been explained in ~~in relation to its preferred~~

~~embodiment~~ a specific EDD reaction, it is ~~to be understood~~ believed that this invention may also be applied in many other possible modifications and variations of chemical processes to fabricate copper layers ~~can be made~~ without departing from the spirit and scope of the invention as hereinafter claimed.